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On the theory of concentration self-quenching by statistical traps

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This work is concerned with the theory of concentration self-quenching of luminescence due to incoherent energy transfer between randomly distributed molecules. A simple model of self-quenching is considered, in which luminescent molecules within a critical distance of each other act as perfect traps. Due to the statistical nature of these traps, few practical results can be obtained from systematic or formal theories. We demonstrate, however, that within the framework of hopping theories for energy transfer an exact and a simple intuitive treatment of the donor and trap distributions differ only very little in their results for the quantum yield and emission anisotropy.

I. INTRODUCTION

Despite years of intensive research and many advances,[1] the theory of incoherent energy transfer in disordered systems still offers several important problems, many of which can be ascribed to the tremendous difficulty of performing the configurational averages needed to connect microscopic solutions of the excitation migration to observable quantities. Although formal and systematic theories[2–9] have yielded valuable insight in the fundamental problems as well as important concrete results, so far, no satisfactory theory[10] has been developed for the high density and (or) long time regime of excitation migration. Also there is, up to now, no practical way of treating systems in which both migration, between donors, and quenching, due to traps, occurs. Therefore, an important role can still be played by simple models of energy transfer. They are approximate usually both in solving the microscopic transport equations and in dealing with configurational averages, but may capture the dominant features over a wide range of densities and (or) times. Pertinent examples are a model introduced by Huber *et al.*,[11] which includes the effects of back-transfer in a pure donor system in a surprisingly accurate manner, and hopping models of energy transfer introduced by Burshtein,[12] which can also deal with donor-trap systems in a practical manner.

Of course, the problem with such simple models lies in the fact, that one has to assess their validity and accuracy by comparison with rigorous results either from theory or from computer simulations. The merits of the model of Huber *et al.* can, for instance, be demonstrated[13] by comparison with the systematic GAF theory.[6] In this work, we present theoretical evidence for the validity of *simple* hopping models applied to self-quenching systems[14–16] in comparison with an *exact* solution within the framework of the hopping theory. In a subsequent paper we present "exact" results for self-quenching obtained from extensive Monte Carlo simulations, which then allow us to assess also the absolute accuracy of hopping models in describing self-quenching systems.

Self-quenching occurs in a system of a single type of luminescent molecules, when two such molecules act as traps for excitation energy upon close approach.[12(b),14–16] The problem is, that these traps are statistical, i.e., that there are inherent correlations between donor and trap positions, since they emerge from a *common* distribution of luminescent molecules. In simple hopping models for self-quenching, we use effectively independent distributions of donors and traps, as if they corresponded to different types of molecules. There is no *a priori* justification for this approximation. It can, however, be provided by deriving, within the framework of hopping theory, exact results for the quantum yield and anisotropy of emission, to which those for the simple model turn out to be surprisingly close.

This paper is laid out as follows. In Sec. II a precise formulation of the problem is given, together with a brief summary of those results of Burshtein's hopping theory needed for our discussion. In Sec. III the results of the previous paragraph are described. Section IV contains a summary and some final remarks. Some technical details are given in the Appendix.

II. DEFINITIONS AND THEORETICAL PRELIMINARIES

Consider a two- or three-dimensional medium in which identical luminescent molecules are embedded at fixed, random positions, with a given number density ρ. These molecules have an electronic excited state with radiative lifetime τ_0, and a total intrinsic lifetime $\tau < \tau_0$, both assumed to be independent of ρ. The excitation energy of this level can be transferred incoherently to any other molecule, at distance r, with an isotropic multipolar transfer rate (strength determined by R_0)

$$w(r) = \frac{1}{\tau_0}\left[\frac{R_0}{r}\right]^m. \tag{2.1}$$

In order to describe self-quenching, we now assume that any two molecules within a fixed distance R_s, the statistical trap radius, of each other, act as traps for the excitations. One may think of this as an extremely simple model for dimerization or excimer formation of two such molecules, which changes their excited state electronic structure thus causing very fast nonradiative decay channels to develop.[16] Mole-

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cules that are not part of such a pair (or even larger cluster) are called donors hereafter.

When molecules in this system are randomly excited at $t = 0$, the subsequent transfer kinetics is described by specifying for each molecule i the probability $p_i(t)$ of being excited at time t. For incoherent energy transfer with a Markovian character, the $p_i(t)$ obey simple coupled rate equations (CRE),

$$\frac{dp_i}{dt} = -\sum_j \mathbb{W}_{ij} p_j(t), \tag{2.2}$$

with i and j running over all donors. $\mathbb{W}$ is the relaxation matrix of the system, given by:

$$\mathbb{W}_{ij} = \delta_{ij} w_i - w_{ji}, \tag{2.3}$$

where w_i is the total transfer rate from donor i to all other donors *and* traps, and w_{ji} is the rate from donor j to donor i. Formally, Eq. (2.2) combined with initial condition $p_i(0) = \delta_{ik}$ is easily solved to yield

$$p_i^k(t) = [\exp(-\mathbb{W}t)]_{ik}. \tag{2.4}$$

This solution has been the starting point of many theoretical approaches in the field,[2,4–9] with the necessity to perform a configurational average of Eq. (2.4) as their common central problem.

One is primarily interested in (i) the configurational average of the probability that an excitation, which was initially created on a donor, is eventually radiated by that or any other donor, and (ii) the average probability that an excitation is radiated from the donor on which it resided initially. These theoretical quantities are closely related to two steady state observables in a typical fluorescence experiment (in which a laser beam, incident along the y axis and polarized parallel to the z axis of the lab frame, excites donors at a constant rate), namely the fluorescence quantum yield and the anisotropy of emission measured along the x axis. To be more precise, we use the following definitions. The fluorescence quantum yield Q is the rate at which excitations are radiated by donors divided by the constant rate of laser induced creation of donor excitations. Thus the quantum yield Q_0 measured in very dilute systems, in which energy transfer plays no role, is τ/τ_0. For the relative quantum yield Q/Q_0, the yield for brevity, one easily derives

$$Q/Q_0 = \tau^{-1}\tilde{N}(\tau^{-1}). \tag{2.5}$$

Here $\tilde{N}(s)$ is the Laplace transform of $N(t)$, the time-dependent donor intensity following δ-pulse excitation at $t = 0$, with the exponential intrinsic decay factored out, so that $N(t)$ solely describes the decay due to transfer. It is instructive to note that the yield equals the fraction of excitations that do not walk into a trap before they decay.[17] The emission anisotropy is defined through

$$A/A_0 = \frac{I_\parallel - I_\perp}{I_\parallel + 2I_\perp}, \tag{2.6}$$

where $I_\parallel$ and $I_\perp$ denote observed donor emission intensities of components parallel and perpendicular to the direction of the laser beam polarization, respectively. As a consequence of the additivity of A [18] for an uncorrelated, isotropic distribution of molecular transition dipoles, and given the isotropic transfer rate, one arrives at

$$A/A_0 = \tilde{N}_0(\tau^{-1})/\tilde{N}(\tau^{-1}). \tag{2.7}$$

Here $N_0(t)$ is the intensity of initially excited donors following δ-pulse excitation at $t = 0$, in other words the configurational average $\langle p_0^0(t)\rangle$ of the conditional probability that an initially excited donor is also excited at time t, again with the intrinsic decay factored out. A_0 denotes the anisotropy at zero density (and equals 0.40). Relation (2.7) is well known for the situation without traps [$N(t) \equiv 1$]; in the presence of traps, the denominator $\tilde{N}$ gives their influence on the total donor intensity, which is proportional to $I_\parallel + 2I_\perp$.[19]

Now $N(t)$ and $N_0(t)$ have to be obtained as suitable averages of the occupation probabilities $p_i(t)$. However, only few fully analytic theories exist dealing with approximate solutions to the CRE in systems with both energy migration and trapping. Among these, Burshtein's theory of energy transfer by means of hopping[12] is particularly attractive for the closeness of its formalism to intuitive ideas about the dynamics of the transfer process. Since the present work elaborates on this theory, we briefly summarize those results that are needed for a self-contained presentation. In Burshtein's derivation of the time-dependent donor intensity $N(t)$, all possible random walks contributing to N are divided into subensembles characterized by the number of hops that are made between donors. Since an exact summation (equivalent to an average) of all contributions in one subensemble is not posssible, the average is approximated by breaking it up into averages over the surroundings of successively visited donors, thus neglecting all correlations between their environments. In this respect the hopping theory is equivalent to the practical implementation[21] of the CTRW-formalism (see, e.g., Ref. 4). Thus, one eventually derives in the Laplace domain

$$\tilde{N}(s) = \frac{\tilde{F}(s)}{1 - \tilde{\Phi}(s)}, \tag{2.8}$$

which leads in the time domain to a convolution-type integral equation with kernel $\Phi(t)$. $\tilde{F}(s)$ and $\tilde{\Phi}(s)$ are, respectively, defined as the Laplace transforms of the functions

$$F(t) = \langle \exp(-wt)\rangle_c \tag{2.9}$$

and

$$\Phi(t) = \langle w' \exp(-wt)\rangle_c. \tag{2.10}$$

Here w denotes the total transfer rate from a given donor to all other donors and traps, and w' the part of this rate to donors alone. $\langle\cdots\rangle_c$ stands for the average over all possible molecular configurations surrounding the central donor. Note, that by neglecting correlations in the environments of donors visited, one rules out the particularly important possibility of back-transfer of the excitation to the molecule it just left. We will therefore call this model the no-back-transfer (nbt) hopping model. Burshtein[12(b)] has also proposed a remedy for this situation, which amounts to the insertion of Huber *et al.*'s well-known back-transfer correction into the hopping theory.[11] Although it is not a systematic correction, one intuitively understands that it takes into account very strong correlations in the environments of successively visit-

ed donors. After the nature of the back-transfer correction (a hyperbolic cosine) we will call this model the cosh-hopping model. With these preliminaries, we can now discuss different ways to apply hopping theory to self-quenching by statistical traps.

III. RESULTS FOR SELF-QUENCHING

Before we present explicit calculations, it is useful to introduce some dimensionless parameters, and to point out some scaling properties. First of all, the critical transfer distance R_0 determines a natural length scale, and from this the reduced density of luminescent molecules is derived: $\hat{\rho} = V_\Delta R_0^\Delta \rho$ (V_Δ denotes the volume of a Δ-dimensional unit sphere). In other words, $\hat{\rho}$ equals the average number of molecules in a sphere with radius R_0. Furthermore, τ_0 provides a natural unit of time. In the absence of other relevant length scales, configurationally averaged quantities depend on density and time only through one scaling parameter $\hat{\rho}(t/\tau_0)^{\Delta/m}$.[13,22] Our trap formation mechanism, however, determines a second length scale, which is most conveniently expressed in dimensionless form: $r_s = R_s/R_0$. Arguments similar to those leading to the above single-parameter scaling, show, that now the time-dependent quantities are functions of two parameters: $\hat{\rho}(t/\tau_0)^{\Delta/m}$ and $\hat{\rho}v_s$, with $v_s = r_s^\Delta$. $\hat{\rho}v_s$ is the average number of molecules in a sphere with radius R_s, and we shall see that it determines the ratio of donor to trap concentrations. It follows that Laplace transforms, and thus steady state quantities, are functions of the system parameters only through $\hat{\rho}Q_0^{\Delta/m}$ and $\hat{\rho}v_s$.

We now turn to explicit calculations. Although in Burshtein's work no expression for $N_0(t)$ was derived, it lies completely within the spirit of this model to approximate this quantity by

$$N_0(t) = F(t). \tag{3.1}$$

The loss of excitation to traps is exactly covered by Eq. (3.1), and again donor–donor transfer is treated in a no-back-transfer approximation. Both the yield and anisotropy are thus determined by $F(t)$ and $\Phi(t)$. The problem in carrying out the involved configurational averages in Eqs. (2.9) and (2.10) for the case of self-quenching stems from the inherent correlations between donor and trap positions, since they are made up by a common distribution of luminescent molecules. In the simplest treatment, we calculate the average probability for a molecule not to have any neighbors within the trap radius R_s. This is easily shown to be $\exp(-\hat{\rho}v_s)$ in the thermodynamic limit. We now think of the system as if it contained independently distributed donors and traps with fixed concentrations. The donors would then have a density

$$\rho_d = \rho \exp(-\hat{\rho}v_s) \tag{3.2}$$

and the remaining particles would be traps, clustered in groups of two or more molecules. Assuming that at moderate densities ($\hat{\rho}v_s$ not too high) the majority of traps occur in pairs, we take as trap concentration,

$$\rho_t = \frac{\rho}{2}\left[1 - \exp(-\hat{\rho}v_s)\right], \tag{3.3}$$

and a doubled donor–trap transfer rate given by

$$w_{dt}(r) = \frac{2}{\tau_0}\left[\frac{R_0}{r}\right]^m. \tag{3.4}$$

We thus treat the two members of a pair as one "quasiparticle," in order to take into account their required closeness. Taking these approximations at face value for the moment, one can easily calculate the relevant transfer quantities, because Eqs. (2.9) and (2.10) can now be worked out by splitting up the averages into a donor and a trap part. One then obtains through standard manipulations

$$F(t) = \exp\{-\Gamma(1-\Delta/m)\left[2^{\Delta/m-1} + \exp(-\hat{\rho}v_s)\times(1-2^{\Delta/m-1})\right]\hat{\rho}(t/\tau_0)^{\Delta/m}\} \tag{3.5}$$

and

$$\Phi(t) = -\frac{\exp(-\hat{\rho}v_s)}{\left[2^{\Delta/m-1} + \exp(-\hat{\rho}v_s)(1-2^{\Delta/m-1})\right]}\times\frac{dF(t)}{dt}. \tag{3.6}$$

For the interesting case of $m = 6$ (Förster rate) and $\Delta = 3$, $\tilde{F}(s)$ can be expressed in terms of the complementary error function, and one finds

$$Q/Q_0 = \frac{\left[1 - \sqrt{\pi}\alpha \exp(\alpha^2)\mathrm{erfc}(\alpha)\right]}{\left[1 - \sqrt{\pi}\beta \exp(\alpha^2)\mathrm{erfc}(\alpha)\right]} \tag{3.7a}$$

and

$$A/A_0 = 1 - \sqrt{\pi}\beta \exp(\alpha^2)\mathrm{erfc}(\alpha), \tag{3.7b}$$

with

$$\alpha = \frac{\sqrt{\pi}}{2}\left[\frac{1}{\sqrt{2}} + \exp(-\hat{\rho}v_s)\left(1 - \frac{1}{\sqrt{2}}\right)\right]\hat{\rho}\sqrt{Q_0} \tag{3.7c}$$

and

$$\beta = \frac{\sqrt{\pi}}{2}\exp(-\hat{\rho}v_s)\hat{\rho}\sqrt{Q_0}. \tag{3.7d}$$

One indeed observes the predicted scaling dependence on the separate system parameters. For other cases, $\Delta/m \neq 1/2$, the Laplace transform must be obtained numerically. Upon insertion of the back-transfer correction, expressions for the cosh-hopping model can easily be obtained. As is well known,[23] working with this back-transfer correction amounts to replacing ρ_d by $\rho_d/2$ and t (in the part of the decay caused by donors) by $2t$. With this prescription one immediately deduces the analogs of Eqs. (3.5) and (3.6) for the cosh-hopping model:

$$F(t) = \exp[-\Gamma(1-\Delta/m)2^{\Delta/m-1}\hat{\rho}(t/\tau_0)^{\Delta/m}] \tag{3.8}$$

and

$$\Phi(t) = -\exp(-\hat{\rho}v_s)\frac{dF(t)}{dt}. \tag{3.9}$$

For $\Delta/m = 1/2$, one finds for the yield and the anisotropy the same expressions as Eqs. (3.7a) and (3.7b), but now with

$$\alpha = \tfrac{1}{2}\sqrt{\pi Q_0/2}\hat{\rho},$$

$$\beta = \tfrac{1}{2}\sqrt{\pi Q_0/2}\exp(-\hat{\rho}v_s)\hat{\rho}.$$

Henceforth we shall concentrate on the nbt-hopping model.

It is clear, that the above separate treatment of donors

and traps is inconsistent with the self-trapping nature of the quenching, since no precautions are taken to avoid that a donor has a neighboring donor, or even a pair, within distance R_s. Consequently, the significance of results [Eqs. (3.5) and (3.6)] is also unclear. We have found, however, that it is possible to perform, within the framework of hopping theory, the configurational averages *exactly, i.e., to all orders in* $\hat{\rho}v_s$. This then also allows us to assess the value of the above approximations.

We return to the original system with one type of luminescent molecules with density ρ, and one form for the transfer rate. For the exact calculation of $F(t)$ from Eq. (2.9), it is not necessary to distinguish between donors and traps, since both contribute in the same way. The central donor just loses its excitation to surrounding particles with concentration ρ, and again standard algebra (see the Appendix) results in

$$F(t) = \exp\{ - [\gamma(1 - \Delta/m, \lambda) - (1 - e^{-\lambda})\lambda^{-\Delta/m}]\hat{\rho}(t/\tau_0)^{\Delta/m}\} \tag{3.10}$$

with $\lambda = (t/\tau_0)r_s^{-m}$. The incomplete γ function arises from the explicit incorporation of an excluded sphere with radius R_s around the excited donor. In Eq. (3.5) even this effect has been neglected. An exact reduction of $\Phi(t)$ from Eq. (2.10) is more involved. First one has to realize that

$$\Phi(t) = \left\langle \sum_{d \neq 0} w_{0d} \prod_{i \neq 0} \exp(-w_{0i}t) \right\rangle_c , \tag{3.11}$$

where d runs over all but the central donor (0) and i over both donors *and* traps. Then, with the aid of the function f_{ij} of the distance between molecules i and j, defined by $f_{ij} = -1$ for $r_{ij} < R_s$ and $f_{ij} = 0$ otherwise, one writes

$$\Phi(t) = \left\langle \sum_{i \neq 0} \left[w_{0i} \prod_{j \neq i} (1 + f_{ij}) \right] \prod_{i \neq 0} \exp(-w_{0i}t) \right\rangle_c . \tag{3.12}$$

Now, no distinction is made anymore between donors and traps in the summation and products. The overlap function $\Pi(1 + f_{ij})$ ensures that traps in the system are being recognized as such. Working out Eq. (3.12) in the thermodynamic limit yields (see the Appendix)

$$\Phi(t) = F(t)\rho \int' d\mathbf{r}_{01} \left\{ w_{01}\, e^{-w_{01}t} \times \exp\left[\rho \int' d\mathbf{r}_{02} f_{12}\, e^{-w_{02}t} \right] \right\} \tag{3.13}$$

with $F(t)$ given by Eq. (3.10). The prime on the integrals indicates the exclusion of the region $r_{0i} < R_s$ from the domain of integration. For a pure donor system, one would have had $\Phi(t) = -dF(t)/dt$, which holds for expression (3.13) without the exponential factor containing the $\mathbf{r}_{02}$ integral [hence $\tilde{N}(s) = 1/s$, or $N(t) = 1$]. The influence of statistical trap formation is thus represented by this factor. After formal Laplace transformation of Eqs. (3.10) and (3.13), one obtains lengthy expressions for $\tilde{F}(\tau^{-1})$ and $\tilde{\Phi}(\tau^{-1})$, which are given in the Appendix. Suffice it to say here, that both $\tilde{F}(\tau^{-1})$ and $\tilde{\Phi}(\tau^{-1})$ can only be calculated by numerical integrations. $\tilde{F}$ can be obtained rather easily in this way, but $\tilde{\Phi}$ involves a rather complicated threefold spatial integral, which in turn occurs inside the time integral associated with Laplace transformation. Therefore, the ensuing numerical integrations, needed to obtain quantitative results, are rather involved.

Explicit calculations have been performed for $\Delta = 3$, $m = 6$, $Q_0 = 1/3$, and two values of r_s, over a density domain that is large enough to follow the decay of donor fluorescence. The case $r_s = 1/7$, together with the other system quantities, may be typical for solutions of chlorophyll a,[15] whereas $r_s = 1/3$ is chosen as a rather large value, in order to follow the extent of the corrections provided by the exact model. The results are summarized in Table I, together with those of the heuristic model [expressions (3.7a)–(3.7d)]. As one might expect, the discrepancies between the exact yield and anisotropy and their values in the heuristic model are largest for $r_s = 1/3$ (at the same reduced density), but in both cases they are very small over the entire physically interesting density regime $\hat{\rho}v_s \lesssim 1$. For higher densities, the deviations in Q/Q_0 increase rapidly, but since by the nature of trap formation values of v_s are expected to be of the order of molecular dimensions, this domain is not of practical importance. We therefore conclude that, surprisingly, the heuristic model gives, within the framework of hopping theory, a good quantitative description of the steady state observables in a self-quenching system.

IV. SUMMARY AND REMARKS

We have justified the use of what *a priori* appears to be a severe simplification of the distribution of donors and statistical traps in hopping models for self-quenching systems. To this end, we compare the quantum yield and the anisotropy of these heuristic models with exact results in the framework of the hopping theory. This greatly increases the usefulness of such heuristic hopping models since one can now apply them to self-quenching systems with more confidence. Having demonstrated the smallness of the discrepancies between exact and heuristic hopping models, one may, *a posteriori*, venture an intuitive explanation for this striking fact by the following arguments. The most severe approximation in the heuristic hopping model seems to be the possibility that the central (excited) donor has a neighboring donor, or even a pair, within distance R_s, which cannot occur in the real system. This would enhance the decay of the excited donors. As is known,[24] however, the inclusion of an excluded sphere (radius R_s) around the central donor only has important effects on the decay for short times, for which $(t/\tau_0)r_s^{-m} \lesssim 1$. More precisely, these exclusion effects are not important for steady state quantities if two conditions are satisfied. (i) $\hat{\rho}v_s \lesssim 1$, which guarantees that the short time interval for which exclusion effects *are* important does not cover the major part of the donor intensity decay. (ii) $r_s^m Q_0^{-1} \ll 1$, which ensures that this short time interval is also small compared to the lifetime τ. For the typical parameters chosen in Sec. III, the second requirement is easily met; the first shows that, indeed, corrections should grow rapidly for $\hat{\rho}v_s \gtrsim 1$, which is however a physically uninteresting density regime.

The fact, that our exact results are only obtained for the nbt-hopping model, is irrelevant to the above conclusion. One can include back-transfer, for instance, by considering the cosh-hopping model. Although a solution of the exact

TABLE I. Comparison of yield and anisotropy for exact and heuristic nbt-hopping models in three dimensions, for two values of r_s at $Q_0 = 1/3$ and $m = 6$.

		Q/Q_0		A/A_0		
	$\hat{\rho}$	Exact	Heuristic	Exact	Heuristic	$\hat{\rho}v_s$
$r_s = 1/7$	1.0	0.997	0.997	0.449	0.448	2.92×10^{-3}
	2.0	0.987	0.987	0.240	0.239	5.83×10^{-3}
	5.0	0.869	0.869	0.740×10^{-1}	0.735×10^{-1}	1.46×10^{-2}
	10.0	0.478	0.478	0.390×10^{-1}	0.385×10^{-1}	2.92×10^{-2}
	20.0	0.108	0.107	0.462×10^{-1}	0.454×10^{-1}	5.83×10^{-2}
	50.0	0.857×10^{-2}	0.821×10^{-2}	0.103	0.101	1.46×10^{-1}
	100.0	0.129×10^{-2}	0.115×10^{-2}	0.196	0.193	2.92×10^{-1}
	200.0	0.226×10^{-3}	0.175×10^{-3}	0.360	0.359	5.83×10^{-1}
	500.0	0.332×10^{-4}	0.182×10^{-4}	0.681	0.700	1.46
$r_s = 1/3$	0.1	1.000	1.000	0.918	0.915	3.70×10^{-3}
	0.3	0.998	0.998	0.780	0.772	1.11×10^{-2}
	1.0	0.970	0.970	0.478	0.465	3.70×10^{-2}
	3.0	0.703	0.691	0.223	0.212	1.11×10^{-1}
	10.0	0.977×10^{-1}	0.842×10^{-1}	0.263	0.257	3.70×10^{-1}
	30.0	0.886×10^{-2}	0.550×10^{-2}	0.581	0.592	1.11
	100.0	0.129×10^{-2}	0.387×10^{-3}	0.946	0.966	3.70

cosh-hopping model apears to be possible in principle, we feel, that solving that model in further support of the conclusion of this work is not worth the effort. After all, the close functional resemblance of a nbt model and a cosh model leads automatically to the same conclusions concerning exclusion effects. Therefore, one expects the heuristic cosh-hopping model also to be very close to its exact analog.

Having assessed the validity of heuristic hopping models in comparison with their exact versions, we will study their absolute accuracy by means of Monte Carlo simulations as part of a subsequent paper.[25]

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APPENDIX

In this Appendix we give some details on the derivation of $F(t)$ and $\Phi(t)$ and the expressions for their Laplace transforms in the exact hopping model.

$F(t)$ describes the decay of the central donor 0 to surrounding donors and traps, which in a nbt model for donor–donor transfer reads

$$F(t) = \left\langle \prod_{i\neq 0} e^{-w_{0i}t} \right\rangle_c = \frac{1}{V^N} \int' d\mathbf{r}_{01}\cdots d\mathbf{r}_{0N} \prod_{i\neq 0} e^{-w_{0i}t}. \tag{A1}$$

Here V denotes the volume of the system and $N+1$ is the total number of molecules (donors *and* traps), which are labeled by i. The region $r_{0i} < R_s$ is excluded from the domain of integration (indicated by the prime on the integrals), since molecule 0 is a donor. As a result of the factorization of the integrand into contributions from separate molecules, one obtains

$$F(t) = \left[\frac{1}{V}\int' d\mathbf{r}_{01}\, e^{-w_{01}t}\right]^N = \left[1 - \frac{1}{V}\int' d\mathbf{r}_{01}(1 - e^{-w_{01}t})\right]^N. \tag{A2}$$

In the last form the thermodynamic limit ($N, V \to \infty$, $N/V = \rho =$ constant) can be taken to yield

$$F(t) = \exp\left[-\rho \int' d\mathbf{r}(1 - e^{-w(r)t})\right]. \tag{A3}$$

Using the transfer rate Eq. (2.1), one now derives Eq. (3.10) through straightforward algebra (see, e.g., Ref. 24). Note that the expressions for the decay in the heuristic models [Eqs. (3.5) and (3.8)] are obtained in a similar way, with adjusted densities and neglect of the cutoff at R_s (i.e., $\lambda \to \infty$).

The derivation of $\Phi(t)$, although more involved, exploits the same methods. Starting from Eq. (3.12), one again expresses the configurational average in terms of integrals, as was done in Eq. (A1). The summation occurring in Eq. (3.12) can be interchanged with the integrations, and one obtains

$$\Phi(t) = \frac{N}{V^N}\int' d\mathbf{r}_{01}\cdots d\mathbf{r}_{0N}\, w_{01}\, e^{-w_{01}t} \times \prod_{i\neq 0,1}\left[(1+f_{1i})e^{-w_{0i}t}\right]. \tag{A4}$$

Again, the integrand factorizes, so that

$$\Phi(t) = \frac{N}{V}\int' d\mathbf{r}_{01}\, w_{01}\, e^{-w_{01}t} \times \left\{1 - \frac{1}{V}\int' d\mathbf{r}_{02}[1 - (1+f_{12})e^{-w_{02}t}]\right\}^{N-1}, \tag{A5}$$

where the integrals for $i \neq 1$ have been rewritten, as before, in order to obtain a form suitable for taking the thermodynamic limit. Working out this limit, one finds

$$\Phi(t) = \rho \int' d\mathbf{r}_{01}\, w_{01}\, e^{-w_{01}t}$$

$$\times \exp\left\{ -\rho \int' d\mathbf{r}_{02} [1 - (1 + f_{12}) e^{-w_{02} t}] \right\}, \tag{A6}$$

which, after using Eq. (A3) gives Eq. (3.13).

Finally, we give the expressions for the Laplace transforms $\tilde{F}(\tau^{-1})$ and $\tilde{\Phi}(\tau^{-1})$. Almost by definition, one obtains

$$\tau^{-1} \tilde{F}(\tau^{-1}) = \int_0^\infty F^*(t) e^{-t} dt, \tag{A7}$$

where $F^*(t) \equiv F(t\tau)$, with F given by Eq. (3.10). Analogously,

$$\tilde{\Phi}(\tau^{-1}) = \int_0^\infty F^*(t) S^*(t) e^{-t} dt, \tag{A8}$$

where $S^*(t) \equiv \Phi(t\tau)/F(t\tau)$ [see Eq. (3.13)], which, e.g., in three dimensions, after exploiting all spatial symmetries, has the complicated form

$$S^*(t) = 3\hat{\rho} Q_0 \int_{r_s}^\infty dr_{01} \left\{ r_{01}^{2-m} e^{-Q_0 t / r_{01}^m} \times \exp\left[-\frac{3}{2} \hat{\rho} \int_{-1}^{+1} dx \int_0^{r_s} dr_{12} r_{12}^2 g_{02} e^{-Q_0 t / r_{02}^m} \right] \right\}, \tag{A9}$$

with $r_{02} = (r_{01}^2 + r_{12}^2 + 2 r_{01} r_{12} x)^{1/2}$, and $g_{02} = 0$ if $r_{02} < r_s$, and $g_{02} = 1$ otherwise.

[1] See, for example, the review articles: D. L. Huber, in *Laser Spectroscopy of Solids*, edited by W. M. Yen and P. M. Selzer (Springer, Berlin, 1981), Chap. 3; A. I. Burshtein, J. Lumin. **34**, 167 (1985), and references therein.
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